# Arene Exchange Reactions of (Arene)tricarbonylchromium Complexes

**T. G. Traylor,* Kevin J. Stewart, and Martin J. Goldberg**

Contribution from the Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093. Received November 7, 1983

Abstract: The kinetics of the reaction of (arene)tricarbonylchromium complexes with arenes have been investigated. The uncatalyzed reaction is first order in complex and first order in arene, indicating a displacement process. The reaction is catalyzed by cyclohexanone in a process which is first order in cyclohexanone and independent of arene concentration. The unreactive (hexamethylbenzene)tricarbonylchromium catalyzes exchange between benzene and (*p*-xylene)tricarbonylchromium, verifying and clarifying the results of Strohmeier. A simplified mechansim is proposed which incorporates the first-order, the second-order, and the catalyzed processes without requiring the production of free tricarbonylchromium.

The formation and displacement of transition-metal π bonds is of great importance in catalysis and of considerable interest in organometallic chemistry.[1–3]

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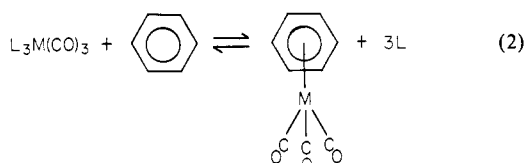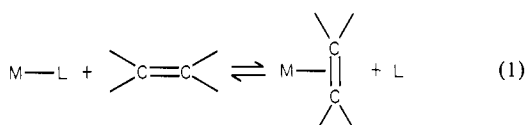
The simple displacement of a σ-bonded ligand by a π-bond ligand, as in eq 1, is understandable as either a dissociative process or an associative nucleophilic displacement.[4,5] The mechanisms by which an arene displaces other ligands or is displaced by three ligands, eq 2, are not so obvious. If three ligands are not to be displaced simultaneously, then intermediates involving partial bonding to the arene are required[3] (eq 3).

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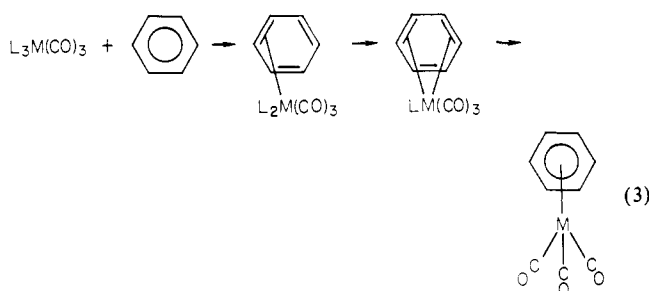
A potentially more complex situation arises in the displacement of one arene by another, illustrated for (benzene)tricarbonylchromium in eq 4. This reaction, which is much slower than a

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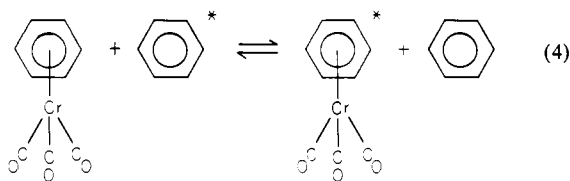
reaction such as eq 1 or reactions of analogous Mo and W complexes, proceeds in the aromatic reagent as solvent with a half-life of many hours at 170 °C.[6–8] Mahaffy and Pauson[8] have studied the equilibria of reaction 4 with a variety of arenes and arene complexes, showing that the stabilities of (arene)tricarbonylchromium complexes decrease in the order

$$Me_6C_6 > \text{mesitylene} > N,N\text{-dimethylaniline} \geq \text{xylene} >$$
$$\text{toluene} \sim \text{benzene} > \text{chlorobenzene} \gg \text{naphthalene}$$

These results agree well with calorimetric measurements which indicated the total arene–metal bond strengths to be 46 ± 3 and 42.5 ± 3 kcal/mol for mesitylene and benzene, respectively.[9]

Strohmeier and co-workers[7] studied the self-exchange of a series of arene complexes or Cr, Mo, and W according to eq 4 where the asterisk represents ^{14}C-labeled arene. Initial rates were measured as functions of initial concentrations of complex, arene, and, in one case, tetrahydrofuran in *n*-heptane solvent. Results were interpreted in terms of eq 5, where X is the reagent arene complex and B is the arene. The first and third terms apply in

$$-d[X]/dt = k_I[X] + k_{II}[X]^2 + k_{II}'[X][B] \tag{5}$$

the cases of naphthalene and cycloheptatriene while the second and third terms are applicable in the isotopic exchange of the toluene, benzene, and chlorobenzene complexes. An approximately 200-fold rate increase is seen upon replacing *n*-heptane by tetrahydrofuran as solvent.[7b]

Mahaffy and Pauson[8] and Willeford et al.[10] later showed that ketones, nitriles, and cyclooctadiene greatly accelerated the rate of reaction 4, even at low concentration. In cyclohexanone solvent, the reaction rate for the benzene complex was faster than that of the mesitylene complex and independent of the displacing arene,

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(6) (a) Sneedon, R. P. A., "Organochromium Compounds"; Academic Press: New York, 1975. (b) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1978**, *19*, 154.

(7) (a) Strohmeier, W.; Mittnacht, H. *Z. Phys. Chem. (Wiesbaden)* **1961**, *29*, 339–346. (b) Strohmeier, W.; Staricco, E. H. *Ibid.* **1963**, *38*, 315–325. (c) Strohmeier, W.; Muller, R. *Ibid.* **1964**, *40*, 85–95.

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hexamethylbenzene, concentration.[10]

Strohmeier proposed, for the rate-limiting steps in the three processes implied by eq 5, the following mechanisms.[7]

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$$(7)$$

$$(8)$$
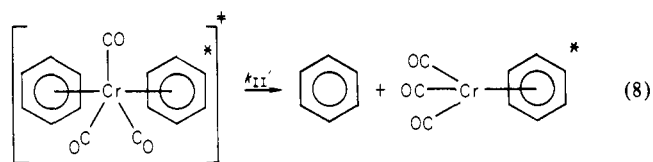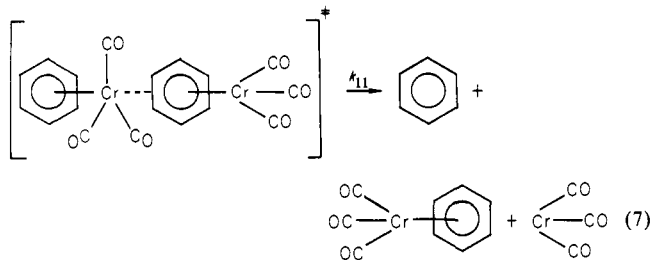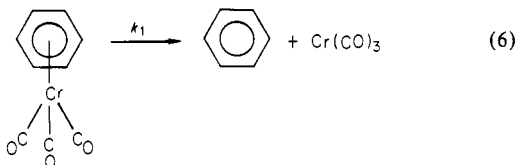
All of these processes have been criticized on energetic grounds by Muetterties[3] and Mahaffy and Pauson.[8] The results of Willeford[10] have been considered inconsistent with those of Strohmeier. However, neither Mahaffy and Pauson nor Willeford et al. have studied the uncatalyzed reaction for which Strohmeier proposed eq 5–8.

Complicating matters further, there remains the possibility of a reversible CO displacement such as is involved in the photochemical process[11,12] (eq 9). It is known that phosphines can thermally replace either CO[8] or the arene.[4,5,8]

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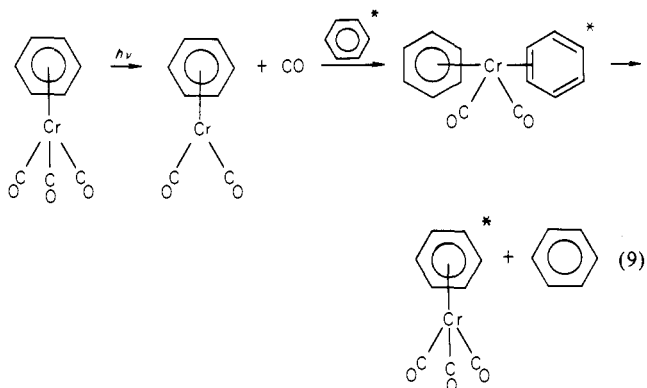
These and other possibilities which constitute the complex maze of possible mechanisms in replacing a six-electron ligand by another six-electron ligand have been outlined in detail by Muetterties.[3]

In order to clarify these apparently inconsistent results and interpretations we have undertaken a kinetic study of the displacement of benzene or substituted benzenes from their chromium carbonyl complexes by other substituted benzenes. The arene exchange reactions were followed by ^{1}H NMR with the disappearance of complex as well as appearance of products being monitored. In this way we can obtain the exact order of the reaction. This could not be done in the initial rate study by Strohmeier with the result that his kinetic terms must be reinterpreted.

Experimental Section

General. Proton NMR spectra were recorded on a Varian EM-390 90-MHz spectrometer. All solution infrared spectra were recorded in 0.11 mm path length CaF$_2$ cells on either a Pye-Unicam 3-200 or Nicolet 7199 infrared spectrophotometer. A Nikon 102 microscope was used in the bead study.

Reagents and Materials. (Arene)tricarbonylchromium complexes used in the kinetic studies were either purchased from Strem Chemicals or synthesized according to literature methods[6b] from Cr(CO)$_6$ (Alfa) and the appropriate arene. Complexes were purified by vacuum sublimation: (benzene)tricarbonylchromium (mp 165–166 °C; NMR (ppm, CDCl$_3$) 5.3 (s, 6 H); IR (cm^{-1}) ν (CO)(CHCl$_3$) 1974, 1896); (p-xylene)tricarbonylchromium (mp 97–98 °C; NMR (ppm, CDCl$_3$) 5.2 (s, 4 H), 2.1 (s, 6 H); IR (cm^{-1}) ν (CO)(CHCl$_3$) 1965, 1889); (mesitylene)tricarbonylchromium (NMR (ppm CDCl$_3$) 5.0 (s, 3 H), 2.2 (s, 9 H); IR (cm^{-1}) ν (CO)(CHCl$_3$) 1963, 1886); (hexamethylbenzene)tricarbonylchromium (mp 230–232 °C, NMR (ppm CDCl$_3$) 2.2 (s, 18 H); IR (cm^{-1}) ν (C-O)(CHCl$_3$) 1949, 1868). Literature values are from references 14–17.

Arene exchange reactions were carried out in 507-PP NMR tubes from the Wilmad Glass Co., Inc. Chemical shifts of reactants and products varied with the amount of arene present and therefore are only reported in CDCl$_3$, which was not used as solvent in the kinetic studies.

Solvents and arene reactants were purified according to literature methods,[18] usually immediately before use. Cyclohexane-d_{12} was 99.5% deuterated and used as purchased from either Sigma or Aldrich.

Precision Sampling Corp. pressure-lok syringes were used to introduce liquid reactants into the reaction vessels. Syringes were weighed before and after addition, and concentrations were calculated by weight.

Copoly(1% divinylbenzene–styrene) beads, 200–400 mesh, were used as received from Bio-Rad Laboratories (see procedures). Infrared spectra of both complexed and uncomplexed beads were taken as KBr pellets. Microanalysis for % Cr in the complexed beads was done by Huffman Laboratories.

Procedure I. Sample Preparation for Rate Constant Determination. Enough reagent (arene)tricarbonylchromium complex was weighed into an NMR tube to afford a concentration of 0.1 M at 0.5 mL of total solution volume. Reagent arene and integrating standard, cyclohexane, where necessary, were then added. Solvent was finally added and the NMR tube immediately attached to the vacuum line. The reaction mixture was then subjected to a minimum of 3 freeze–pump–thaw cycles to degas the solution. The NMR tube was then sealed under vacuum.

Rate Constant Determination. The samples prepared in the above manner were reacted at 170 °C. The reactions were followed by integrating the complexed and free arene proton resonances, aromatic and methyl when possible, at various times during the exchange. The reactions were quenched simply by removing the tube from the 170 °C bath for analyses and then returning it to the bath. Mass balance or an internal standard was employed to convert integrations into concentrations. Each resonance of interest was integrated a minimum of eight times, with the average value used in calculating the rate constant. All reactions exhibited normal first-order kinetics over the 20–70% exchange examined. In some cases where the reactions were very slow, oxidative decomposition over the long reaction times limited the extent of reaction examined to 1 half-life. First-order rate constants were calculated as the slope of the first-order kinetic plots for appearance of product complex and disappearance of reactant complex using a modified least-squares program. Second-order rate constants were calculated as the slope of the plot of concentration vs. first-order rate constants with a least-squares program. At least six data points were used for every plot with the standard deviation of the line appearing as the confidence limit on the rate constant.

Procedure II. Synthesis of Copoly(1% divinylbenzene–styrene)tricarbonylchromium(0). Ten grams of the copoly(1% divinylbenzene–styrene) beads were added to 250 mL of di-n-butyl ether in a 500-mL round-bottom flask. Argon was bubbled through the mixture for 15 min. Tetrahydrofuran (25 mL) was then added and the mixture refluxed for 20 h under a positive pressure of argon and then cooled to room temperature. Hexacarbonylchromium (45 mmol) was added to the reaction mixture which was then subjected to 5 freeze–pump–thaw cycles. The reaction mixture was then slowly brought to reflux under a positive pressure of argon. The mixture began to turn light yellow after 1 h and

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Table I. Conditions for Arene and ^{13}CO Exchange upon Heating a 0.05 M Solution of ^{13}CO-Labeled (Benzene)tricarbonylchromium at 170 °C

sample no.	heating time,[a] h	solvent	[mesitylene], M	[acetone-d_6], M	IR of recovered complexes	^{13}CO exchange	$Cr(CO)_6$ formed
1	226	mesitylene	7.2	0	(1972, 1963, 1948, 1928 sh)[b] [1950, 1935, 1917, 1865][c]	yes	*d*
2	42.5	mesitylene	7.1	0.20	(1962, 1950, 1928, 1875, 1858)[b] [1950, 1935, 1917, 1863, 1844][c]	no	no
3[e]	38.6	mesitylene	7.2	0	(1962, 1950, 1928, 1875, 1858)[b] [1950, 1936, 1917, 1863, 1844][c]	no	yes
4	42.5	cyclohexane-d_{12}	0	0.20	(1962, 1950, 1928, 1875, 1858)[f]	yes	no
5	226	cyclohexane	0	0	2011, 1974, 1963, 1893, 1858[f]	much	yes
6	226	cyclohexane[g]	0	0	1962, 1950, 1928, 1875, 1859[h]	no	no

[a] Samples, 1, 2, and 3 were found to be converted 75%, 69%, and 34%, respectively, to (mesitylene)tricarbonylchromium. [b] (Benzene)tricarbonylchromium isolated by HPLC. [c] (Mesitylene)tricarbonylchromium isolated by HPLC. [d] Not analyzed. [e] 0.10 M ^{13}CO-labeled (benzene)tricarbonylchromium. [f] Isolated but not separated complexes. [g] No ^{13}CO added. [h] This spectrum was superimposable with that of the starting material.

was refluxed a total of 48 h after which the stirred solution was a rich yellow. The mixture was then permitted to slowly cool to room temperature with the condenser being shut off so the unreacted $Cr(CO)_6$ would distill out. The bright yellow beads were filtered on a sintered glass filter, washed several times with degassed THF, and dried under high vacuum for 15 h. The complexed beads were stored under argon until use (% Cr 8.23; ν (CO)), 1965, 1875 cm^{-1} (lit.[19] 1965, 1880).

Three-Phase Test.[13] Fifty milligrams each of complexes and uncomplexed beads were mixed thoroughly in a small mortar. The uncomplexed beads used here had been washed with degassed CH_2Cl_2 and dried in vacuo. Approximately 30 mg of the bead mixture was weighed into a Pyrex tube. The bead mixture, in the tube, was then put under high vacuum ($\sim$0.005 mmHg) for 5–10 min and then under argon. Ten microliters of a possible ligand (e.g., pentanonitrile) was added to the tube and washed down with 240 μL of cyclohexane solvent. The heterogeneous reaction mixture was then subjected to a minimum of 3 freeze–pump–thaw cycles. The tube was then sealed under vacuum. The beads and ligand were reacted at 170 °C for 48 h after which the tube was opened, solvent removed under vacuum, and beads dried under vacuum Random samples of the dried beads were then viewed under the microscope at 100× magnification. A positive test for exchange was indicated by the absence of any white beads. In addition, some of the beads were placed on a glass slide and heated in an oven at 100 °C for several hours. These beads were then viewed under the microscope, revealing only green beads if exchange had occurred. Cyclohexane was chosen as solvent since no bead exchange occurred in a tube with only cyclohexane after 70 h at 170 °C.

Preparation of ^{13}CO-Enriched (Benzene)tricarbonylchromium. (Benzene)tricarbonylchromium (0.08 g, 37.7 mmol) was added to 10 mL of THF in a 25-mL round-bottom flask containing a magnetic stir bar and equipped with a 14/20 vacuum adapter. The solution was subjected to 5 freeze–pump–thaw cycles prior to warming to room temperature and introduction of ^{13}CO. After introduction of ^{13}CO, the adapter was closed and the solution photolyzed for 16 h in a Rayonet UV photochemical reactor equipped with a magnetic stirrer. Upon completion of the photolysis, the solution was filtered through glass wool (to remove Cr(III) oxidative decomposition products) and the THF evaporated under high vacuum leaving a yellow residue of (benzene)tricarbonylchromium. The labeled (benzene)tricarbonylchromium was purified by vacuum sublimation: yield 47.7 mg (59% yield); mp 160–161.5 °C (lit.[14] mp 165.5–166.5 °C); ^{1}H NMR (C_9H_{12}, 25 °C, 90 MHz) δ 4.8 (s, 6 H); IR ($CDCl_3$ 0.11 mm CaF_2) ν (CO) 1962, 1949, 1928, 1875, 1858 cm^{-1}, Figure 1; MS (70 eV), m/e 217 (5.1), 216 (8.5), 215 (7.2), 214 (2.4), 130 (30.5), 52 (100).

Arene and ^{13}CO Exchange Studies. NMR tubes were charged with the ^{13}C-labeled benzene complex (0.05 M) and the reagents shown in Table I. After 5 freeze–pump–thaw cycles the tubes were brought to 1 atm with ^{12}CO and sealed off, leaving a total of (bound and free) ^{12}CO to ^{13}CO ratio of 4.4 to 1. Sample tubes 1 and 2, containing mesitylene, were removed at intervals and NMR spectra taken to indicate the extent of reaction as described in Table I. Plots of ln of reactant or product concentration as determined by this NMR method against time afforded the rate constants.

At the end of the heating time, 0.3–0.5-μL samples of the solutions were injected into the gas–liquid chromatograph equipped with a Supelco Inc. $^1/_4$-in. o.d., 2-mm i.d. glass column packed with 3% SE-30 on 100/120 mesh Supelcoport. Conditions were the following: helium flow rate 30 mL/min, synthetic air flow rate 60 mL/min, hydrogen flow rate
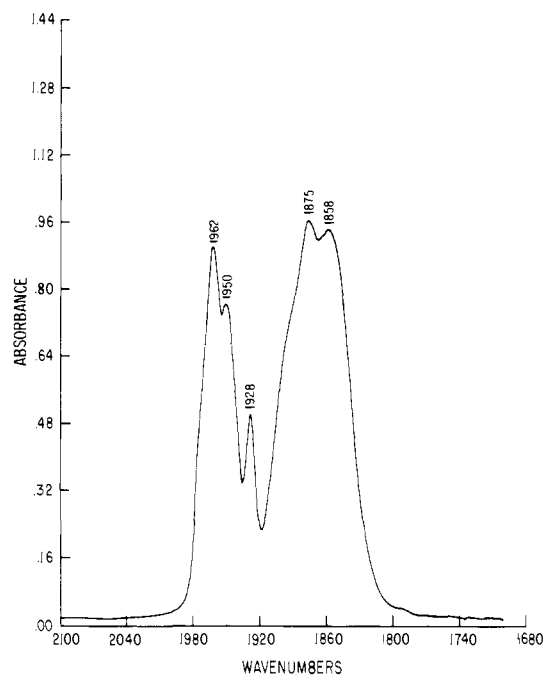
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Figure 1. FTIR spectra of (benzene)tricarbonylchromium after 16 h of photolysis in the presence of ^{13}CO.

30 mL/min, injector temperature 209 °C, F.I.D. temperature 229 °C, column temperature 170 °C. Retention times were the following: solvent and benzene, 0.34 min; mesitylene, 0.45 min; (benzene)tricarbonylchromium, 1.93 min; (mesitylene)tricarbonylchromium, 3.09 min. Selected integrated peaks were divided by the total area of all peaks of Cr species to obtain relative concentrations, from which rate constants were calculated.

FTIR Analyses. After the heating period, samples 3, 4, and 5 were diluted with $CDCl_3$ and the FTIR determined, using 32 to 256 scans. Samples 1 and 2 were separated into the benzene complex and mesitylene complex by HPLC (described below) and the FTIR of the individual components determined. Comparisons of these IR spectra with that of the ^{13}CO-labeled starting compound and with those of pure unlabeled complexes revealed the extent of ^{13}CO to ^{12}CO exchange.

The extent of hexacarbonylchromium production in sample 5 was estimated by subtracting alternatively the spectra of pure hexacarbonyl or pure benzene complex from that of the product and comparing the two difference spectra. This procedure revealed about 40% each of unlabeled and monolabeled (benzene)tricarbonylchromium and 15% hexacarbonylchromium.

HPLC Separation. Samples 1 and 2 were diluted with 1:1 hexane: ethyl acetate and separated on a Waters analytical μ-porasil column. Conditions were the following: pump speed, 3 mL/min; elutant, 98:2 hexanes:ethyl acetate; detector, variable wavelength set at 325 nm. Mesitylene eluted first (1 min) followed by mesitylene and benzene complexes (2 and 3 min, respectively).

Results

The uncatalyzed reactions were carried out at 170 °C in sealed NMR tubes and the concentrations of reactants and products
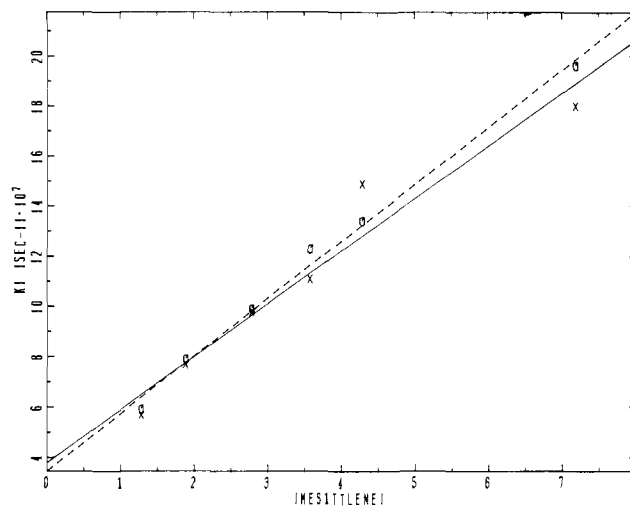
Figure 4. k_{obsd} for arene exchange between the benzene complex and mesitylene at 170 °C as a function of mesitylene concentration. k_{obsd} from production of free benzene (X) and k_{obsd} from production of (mesitylene)tricarbonylchromium (□).
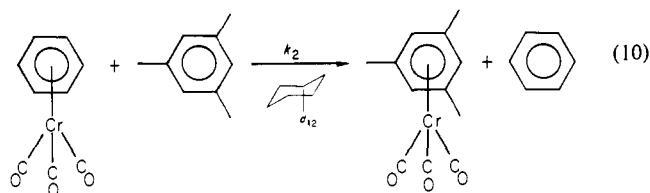
Table II. Rate Constants for the Reaction of Mesitylene with 0.1 M (Benzene)tricarbonylchromium in Cyclohexane-d_{12} at 170 °C

[mesitylene], M	$10^{-7}k_{obsd}$,[a] s^{-1}	$10^{-7}k_{obsd}$,[b] s^{-1}
7.2	18.0 ± 0.6	19.6 ± 0.8
4.3	14.9 ± 0.4	13.4 ± 1.2
3.6	11.1 ± 0.6	12.3 ± 0.9
2.8	9.8 ± 0.4	9.9 ± 0.5
1.9	7.7 ± 1.4	7.9 ± 1.9
1.3	5.7 ± 0.4	5.9 ± 0.6
0.6[c]	3.3 ± 0.2	

[a] Rate constants were obtained from rate of appearance of free benzene. [b] Rate constants were obtained from rate of appearance of (mesitylene)tricarbonylchromium. [c] Free mesitylene aromatic protons used as internal standard.

concerning product structure. The NMR spectra of a solution of 0.1 M benzene complex in mesitylene (solvent) at 0, 83, and 139 h are shown in Figure 2. Plots of the appearance of free benzene and (mesitylene)tricarbonylchromium as first-order processes for the reaction of 0.1 M (benzene)tricarbonylchromium with 7.2 M mesitylene are shown in Figure 3. The rate constants obtained by the two measurements agree within ±10% in this and in all other kinetic determinations of the series. If a reaction showed appreciable oxidative decomposition, these two measurements differed and green oxidation products appeared in the reaction mixture.

A plot of the first-order rate constants for this reaction, eq 10, as a function of initial concentration of mesitylene, using data from Table II, appears in Figure 4. The slopes, from the two analytical

Figure 2. Proton NMR spectra of a solution of 0.1 M (benzene)tricarbonylchromium in mesitylene (solvent) at 0, 83, and 139 h of heating at 170 °C.
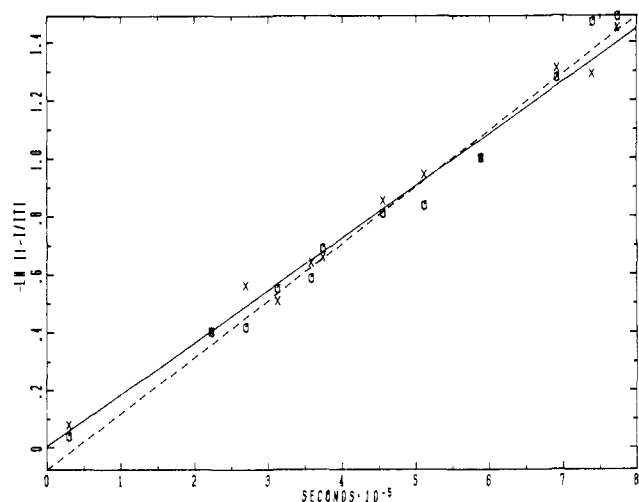
Figure 3. First-order kinetic plot for the production of (mesitylene)tricarbonylchromium (□) and free benzene (X) for arene exchange between 0.1 M (benzene)tricarbonylchromium and mesitylene (solvent) at 170 °C.

monitored by multiple integrations at each time in the rate determination. The use of an added internal integration standard was common as was using mass balance as standard in cases where it was possible. The method is not very accurate, but it is definitive

(10)

procedures discussed above, yield second-order rate constants of $2.1 \pm 0.3 \times 10^{-7}$ and $2.3 \pm 0.1 \times 10^{-7}$ M^{-1} s^{-1} for appearance of free benzene and the mesitylene complex, respectively. These results clearly demonstrate the first-order dependence on arene. The intercept values of 3.8×10^{-7} and 3.5×10^{-7} s^{-1}, respectively, represent the rate constant for another process, either a first-order dissociation process or a process which is bimolecular in complex, as suggested by Strohmeier. The second mechanism will be discussed later.

Cyclohexanone Catalysis. In order to understand the rapid arene exchange in cyclohexanone reported by Willeford et al.,[10]

Arene Exchange Reactions

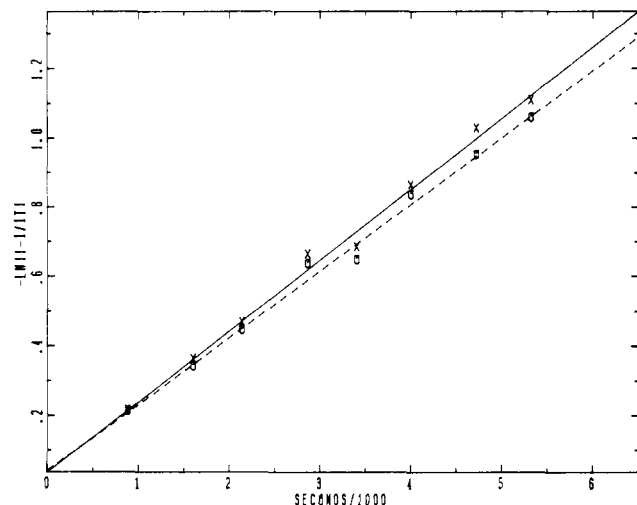*J. Am. Chem. Soc., Vol. 106, No. 16, 1984* 4449

Figure 5. First-order kinetics plot for the production of free benzene (X) and production of (mesitylene)tricarbonylchromium (□) for arene exchange between 0.1 M (benzene)tricarbonylchromium and mesitylene (solvent) in the presence of 0.77 M cyclohexanone at 170 °C.

Table III. Rate Constants for the Reaction of 0.1 M (Benzene)tricarbonylchromium with Mesitylene at 170 °C in Mesitylene Containing Cyclohexanone

[cyclohexanone], M	$10^{-5}k_{obsd}$,[a] s^{-1}	$10^{-5}k_{obsd}$,[b] s^{-1}
1.15	33.7 ± 1.1	32.7 ± 1.1
0.96	23.4 ± 0.9	24.5 ± 0.8
0.77	20.4 ± 0.7	19.2 ± 0.7
0.58	17.4 ± 0.9	17.7 ± 1.7
0.38	10.0 ± 0.3	10.1 ± 0.4
0.19	5.7 ± 0.8	5.0 ± 0.4
0.19[c]	4.8 ± 0.2	4.7 ± 0.4
0.19[d]	5.7 ± 0.4	5.6 ± 0.2

[a] Rate constants were obtained from appearance of free benzene. [b] Rate constants were obtained from appearance of (mesitylene)tricarbonylchromium. [c] 2.0 M mesitylene; cyclohexane solvent. [d] 1.0 M mesitylene; cyclohexane solvent.

we have studied the exchange reaction in dilute cyclohexanone. To compare with our other results, we determined the rates of the exchange reaction of (benzene)tricarbonylchromium in mesitylene solvent, justified below, in the presence of varying concentrations of cyclohexanone. A first-order plot of the reaction containing 0.77 M cyclohexanone is shown in Figure 5. A plot of the first-order rate constants from similar plots as a function of cyclohexanone concentration, using data from Table III, appears in Figure 6. The plot demonstrates a first-order dependence on cyclohexanone and affords a second-order rate constant, same for both measurements, $k_2 = 2.7 \times 10^{-4}$ M^{-1} s^{-1}.

The dependence of the cyclohexanone-catalyzed process on arene at the lowest cyclohexanone concentration, 0.19 M, was determined by varying the concentration of mesitylene from 1.0 to 7.2 M. No measurable effect on the rate was seen. These results are included in Table III.

The cyclohexanone-catalyzed reaction is therefore first order in (arene)tricarbonylchromium, first order in cyclohexanone, and zero order in arene, agreeing with and extending Willeford's results.

(Arene)tricarbonylchromium Catalysis. In order to understand Strohmeier's report[7] of a rate component second order in (arene)tricarbonylchromium complex (eq 5) we have chosen as a possible catalyst a second complex which is relatively inert toward exchange itself[8] (hexamethylbenzene)tricarbonylchromium. The exchange reaction studied is displacement of *p*-xylene from its tricarbonylchromium complex by benzene, using *p*-xylene as solvent (eq 11).[20] This choice was made for analytical reasons as the ¹H NMR resonances of the reactants and products are more clearly separated. The first-order rate constants were determined
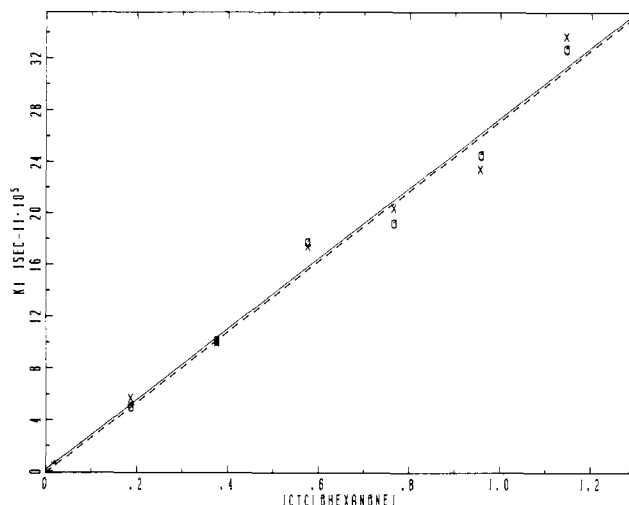
(20) Traylor, T. G.; Stewart, K. J. *Organometallics* **1984**, *3*, 325.

Figure 6. The observed first-order rate constants for arene exchange between (benzene)tricarbonylchromium and mesitylene in the presence of cyclohexanone at 170 °C as a function of cyclohexanone concetnration. k_{obsd} from production of benzene (X) and k_{obsd} from production of (mesitylene)tricarbonylchromium (□).
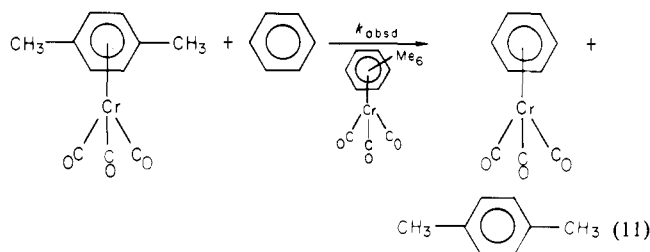
by both the appearance of products of the exchange and disappearance of reactant complex. The similarity of the rate constant values from the different measures of the rate of exchange, especially the rates of production of free arene methyl protons which varied only slightly at the higher concentrations of hexamethylbenzene complex, verified the hexamethylbenzene complex was relatively inert toward exchange while catalyzing the exchange of the *p*-xylene complex.

The rate constants, when plotted as a function of (hexamethylbenzene)tricarbonylchromium concentration,[20] demonstrate a first-order dependence on the complex. The slope of this plot affords the k_{II} of eq 5 for this process, represented in eq 12, k_{II} = 5.5 × 10⁻⁶ M⁻¹ s⁻¹. Hexamethylbenzene complex concentration
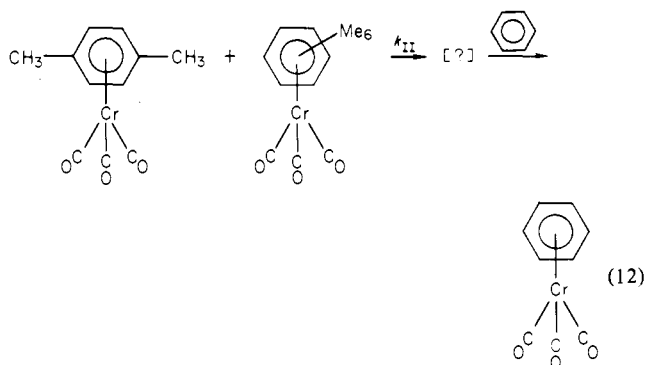
was not varied over 0.18 M, since at higher concentrations the complex was not entirely in solution at the temperature at which the NMR spectra were recorded.

Three-Phase Test for Dissociative Exchange Processes. The three-phase test[13] using polystyrene beads is ideally suited for this study since the beads are easily converted into the reagent by treatment with hexacarbonylchromium in the usual way.[6b] In our application the question asked is whether a tricarbonylchromium, dissociated from its parent arene, has a sufficient lifetime to diffuse

Table IV. Test for Exchange of the Tricarbonylchromium Unit from One Polystyrene Bead to Another after 48 h at 170 °C in Cyclohexane Solvent

catalyst	[catalyst], M	exchange (+) or no exchange (−)
1,5-COD	0.33	(+)
pentanenitrile	0.39	(+)
THF	0.41	(+)
triphenylphosphine oxide	0.10	(+)
pyridine[a]	0.50	(+)
ethyl acetate	0.41	(+)
cyclohexanone	0.39	(+)
di-n-butyl ether	0.24	(−)
cyclohexane	9.25	(−)

[a] Lower temperature used due to oxidative decomposition at 170 °C.

some distance in solution. The experiment is a qualitative one in which a set of polystyrene beads, 1% cross-linked with 200-μm diameters, were divided into two parts. One part was exhaustively treated with hexacarbonylchromium at high temperature[6b] and evacuated to remove excess hexacarbonylchromium. These beads are bright yellow and turn dark green when heated to 100 °C in air. The yellow beads were mixed with an equal amount of the original, but solvent extracted, beads in cyclohexane with or without catalyst and after careful degassing heated for 48 h at 170 °C. The beads were then cooled, dried, and examined under the microscope before and after heating in air. Those beads which exchanged had become uniformly yellow and those which did not exchange could easily be discerned to be mixtures of white and yellow beads. Other analytical methods were not required to determine whether facile dissociative reaction had occurred.

Table IV lists conditions for the test and indicates whether bead-to-bead exchange occurred. The table also shows that in cyclohexane alone or with added di-n-butyl ether, no exchange occurred. However, the catalysts used by Mahaffy and Pauson[8] brought about rapid exchange. In the case of pyridine, the intermediate trisligand complex (λ_{max} ~390 nm) was observed to accumulate in the solvent.

Effects of Added CO on Arene Exchange. (Benzene)tricarbonylchromium, a mixture of mono-, di-, and tri-[13]CO-labeled complexes (see Figure 1), was heated to 170 °C under 1 atm of [12]CO for various times in the presence and absence of mesitylene and acetone as outlined in Table I. The first-order rate constant for mesitylene formation was 1.7×10^{-6} s^{-1} in pure mesitylene and 8×10^{-6} s^{-1} in mesitylene containing 0.2 M acetone, with both rates determined as described above. The uncatalyzed rate constant is within experimental error of the corresponding rate in the absence of CO recorded in Table II for the reactions in pure mesitylene.

Both (benzene)tricarbonylchromium and (mesitylene)tricarbonylchromium were isolated after 39 h (34% conversion) and 226 h (75% conversion) in the uncatalyzed reaction and after 42.5 h (69% conversion) in the catalyzed reaction (Table I). The infrared spectra of the products from the catalyzed reaction (sample 2) are compared with that of the starting material in Figure 7. The IR of recovered benzene complex is almost identical with that of the starting material. Furthermore, the recovered mesitylene complex is also essentially identical except for shifts of all peaks by about 13 cm^{-1}. These reactions occurred with no CO exchange.

By contrast, the recovered benzene complex from heating the starting material under the same conditions, except that mesitylene was replaced by cyclohexane, showed loss of about half the tri-labeled complex and appearance of the unlabeled complex (sample 4, Figure 8). Thus mesitylene retards CO exchange.

The uncatalyzed reaction (sample 3) was heated at 170 °C until about 34% conversion to (mesitylene)tricarbonylchromium. The recovered complexes are compared with the starting material in Figure 9. The recovered (benzene)tricarbonylchromium shows no appreciable loss of the triply labeled species (at 1928 cm^{-1}). At 75% reaction the uncatalyzed process shows some loss of the triply labeled species, probably through direct CO exchange of starting material (sample 1, Figure 10). These differences indicate
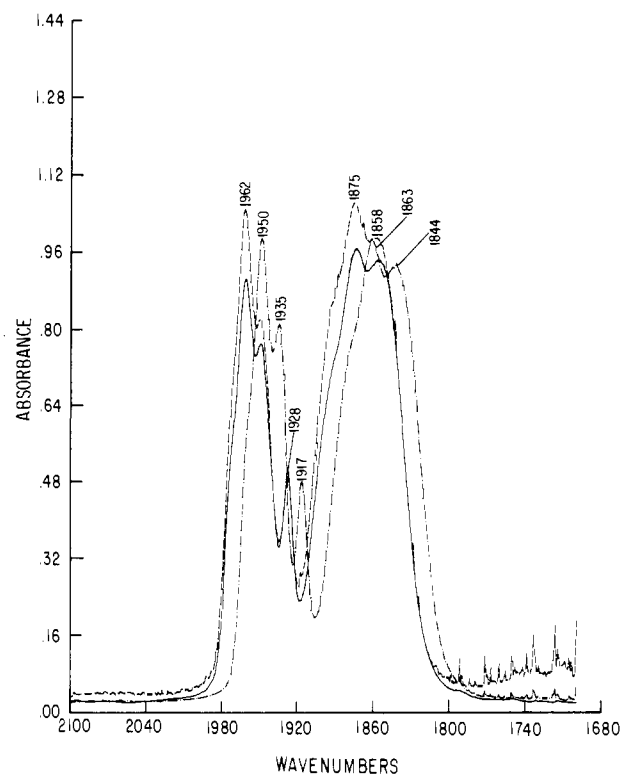

Figure 7. Composite spectra for catalyzed exchange of [13]CO-labeled complex under 1 atm of [12]CO (Table I) showing starting material (—), recovered (benzene)tricarbonylchromium (– – –), and recovered (mesitylene)tricarbonylchromium (– · –).
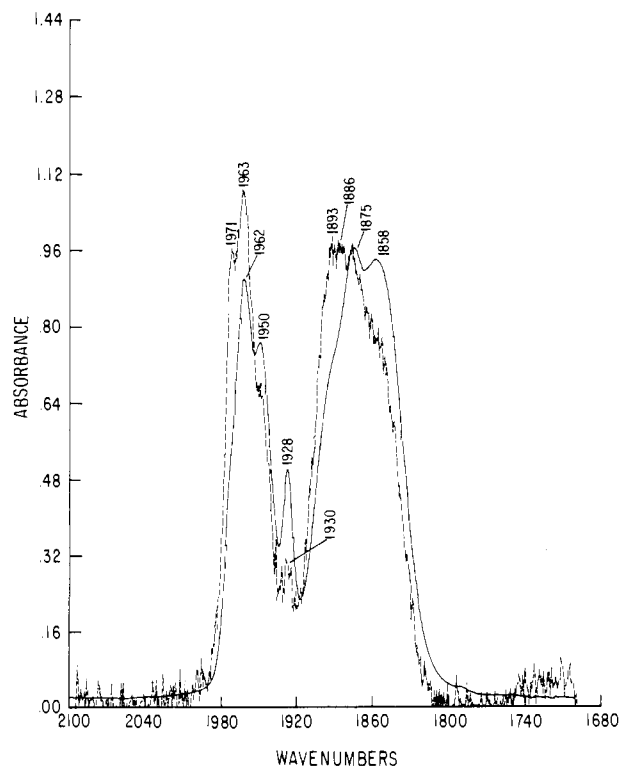

Figure 8. IR spectra comparing starting material (—) and (benzene)-tricarbonylchromium (– – –) recovered from catalyzed reaction in the absence of mesitylene. See Table I.

that the [12]CO labeling process occurs at a slower rate than does arene exchange. This is especially striking when compared to the same reaction in which cyclohexane replaces mesitylene (sample 5, Figure 11). In this case all the triply labeled complex is lost and a large amount of PhHCr([12]CO)$_3$ is formed along with Cr-(CO)$_6$. This can be clearly demonstrated by subtracting the spectra of the starting material and the pure [12]CO complex from

Arene Exchange Reactions
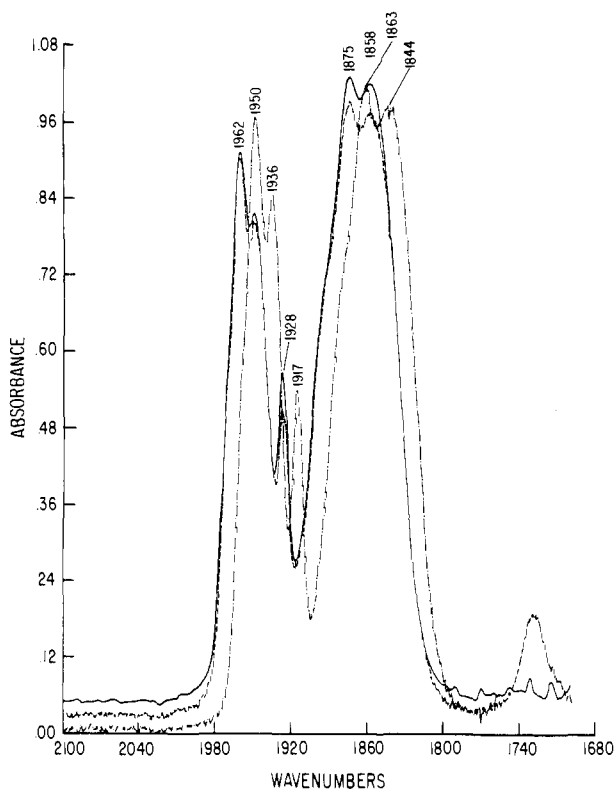
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Figure 9. Spectra comparing (benzene)tricarbonylchromium (- - -) and (mesitylene)tricarbonylchromium (- · -) isolated after 34% uncatalyzed arene exchange with that of the labeled starting material (—).
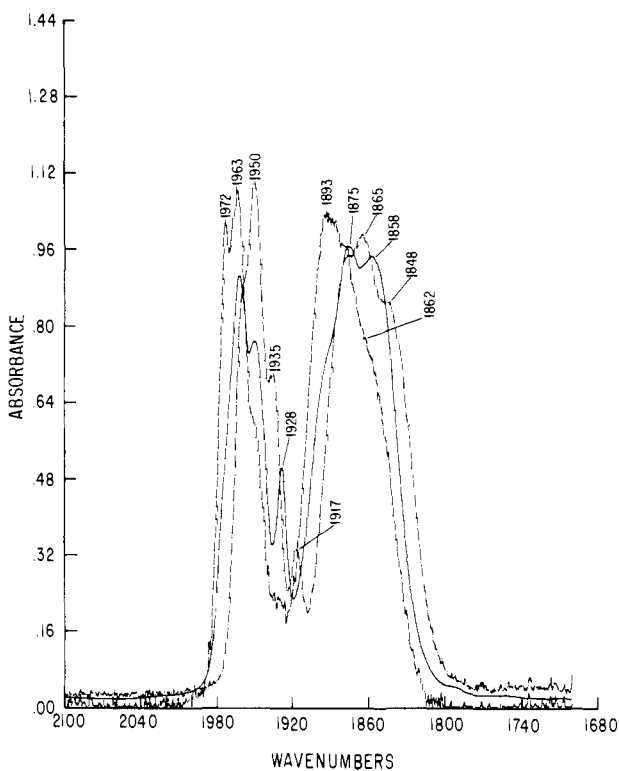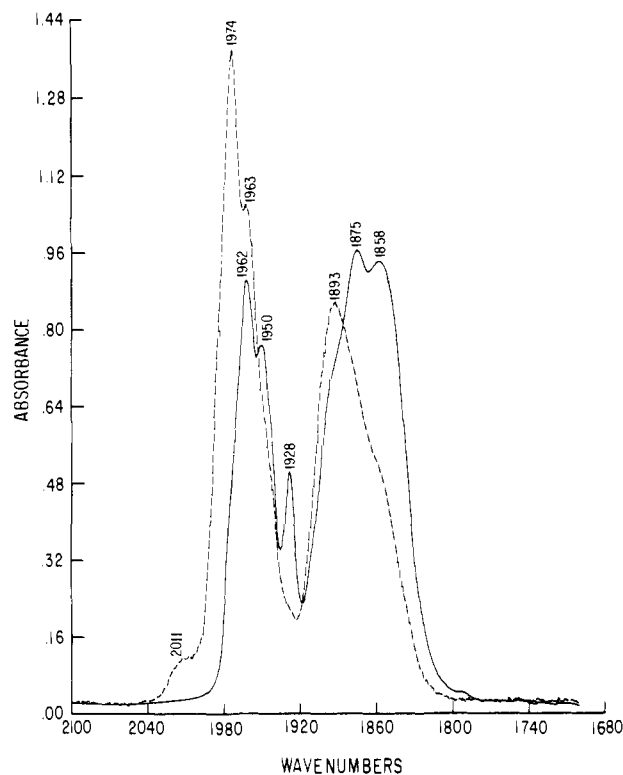

Figure 11. Spectra of starting complex (—) and material recovered (- - -) from uncatalyzed exchange reaction in the absence of mesitylene, showing hexacarbonylchromium (2011, 1974 cm^{-1}) and unlabeled (benzene)tricarbonylchromium (1963, 1893 cm^{-1}). See Table I.

mechanisms of the exchange in detail, it is instructive to compare experimental results obtained here and in the other kinetic studies. This is pertinent because Strohmeier's results have been stated to be in conflict[8] with those of Willeford.[10] Strohmeier reported values of k_{II}', eq 5, for the reaction of (benzene)tricarbonyl-chromium with ^{14}C-labeled benzene of 1×10^{-7} M^{-1} s^{-1} and a value of 2.5×10^{-7} M^{-1} s^{-1} for the isotopic toluene exchange. Figure 4 reveals a second-order rate constant for mesitylene reacting with (benzene)tricarbonylchromium of 2.1×10^{-7} M^{-1} s^{-1}, in excellent agreement with Strohmeier's value. Strohmeier's k_{II} value for the term second order in (benzene)tricarbonylchromium is 1.5×10^{-6} M^{-1} s^{-1}, and k_{II} for the toluene case is 3×10^{-6} M^{-1} s^{-1}. We observed a second-order rate constant for the reaction of (hexamethylbenzene)tricarbonylchromium with *p*-xylenetri-carbonylchromium of 5×10^{-6} M^{-1} s^{-1},[26] again in excellent agreement with the reported value considering that the alkyl-benzenes are different and that both the experimental procedures and kinetic analyses are different.

In order to compare results with Willeford et al.,[10] we calculate, from their results, the second-order rate constant for their reaction of cyclohexanone solvent with (benzene)tricarbonylchromium at 170 °C to be 4×10^{-4} M^{-1} s^{-1} compared to our value of 2.7×10^{-4} M^{-1} s^{-1} obtained at low cyclohexanone concentration from Figure 6. This is also in excellent agreement considering the rather large temperature extrapolation of the rate constant in pure cy-clohexanone.

There is therefore no conflict between the results of Strohmeier and Willeford. We have confirmed the experimental findings of Strohmeier. Their interpretation will be discussed below.

Uncatalyzed Exchange Reactions. Kinetics of uncatalyzed exchange reactions have not been reported since the work of Strohmeier.[7] We report, in Figure 4, the observed first-order rate constants for the exchange reaction of (benzene)tricarbonyl-chromium with mesitylene in cyclohexane at 170 °C as a function of mesitylene concentration. The slope of this plot, excluding the rate at 0.6 M mesitylene which will be discussed later, gives second-order rate constants of 2.1 ± 0.3 and $2.3 \pm 0.1 \times 10^{-7}$ M^{-1} s^{-1}, depending upon whether benzene or (mesitylene)tricarbo-nylchromium is used for analysis. The intercept of this plot, though inaccurate, is about 3×10^{-7} s^{-1}. If interpreted as $k_{II}[X]$ according

Figure 10. Spectra comparing (benzene)tricarbonylchromium (- - -) and (mesitylene)tricarbonylchromium (- · -) isolated from the uncatalyzed exchange reaction (75% conversion) with that of the labeled starting material (—). See Table I.

that of the product. Again, mesitylene retards CO exchange. We conclude that in neither catalyzed nor uncatalyzed arene exchanges is CO exchange directly involved.

Discussion

Comparison of Experimental Results. Before discussing

to the Strohmeier rate law, e.g., eq 5, this gives a $k_{II} \sim 3 \times 10^{-6}$ $M^{-1} s^{-1}$, also in good agreement with his results.

The similarity of our result, $2 \times 10^{-7} M^{-1} s^{-1}$, and the isotopic benzene exchange rate constant or Strohmeier et al.,[7a] 9.8×10^{-8}, suggests the electronic effect of the entering arene is rather small.[21] These and previous results clearly show a simple displacement reaction.

We and others[3,8] find the uncatalyzed dissociation of $Cr(CO)_3$ to be a rather unlikely process. The three-phase test, discussed previously, indicates no exchange in hydrocarbon solvents, eq 13.

$$ (13) $$
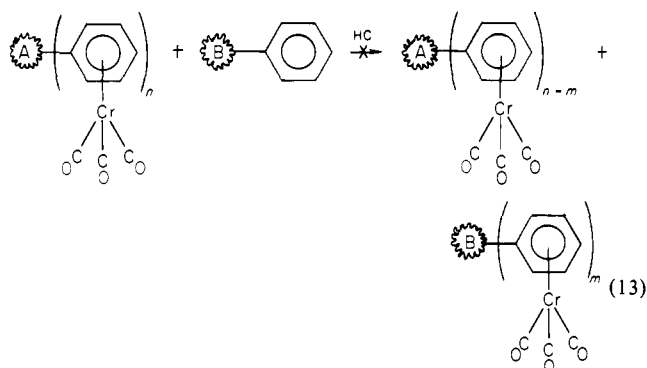
Jackson et al.[22] reported that the (*cis*- or *trans*-1-methyl-indane)tricarbonylchromium compelxes do not isomerize in decalin at 170 °C for 21 h, conditions where arene exchange, extrapolated to zero arene concentration, as in Figure 4, would proceed 1.5%. This experiment is therefore not definitive. Similarly, the same test repeated by Pauson and Mahaffy[8] in the presence of mesitylene is not definitive because the solvent was acetone and the temperature and time were such that no uncatalyzed process occurred. The three-phase test is also not very definitive because unsaturated chromium carbonyls react very rapidly and might not diffuse the required distances.[23] Nevertheless, this dissociation seems chemically rather unreasonable.

Involvement of CO in Arene Exchange. We have shown in Figures 7–11 that the $Cr(^{13}CO)_3$ group can be transferred from one arene to another intact and that added CO neither retards nor accelerates arene exchange. These findings seem to eliminate reversible CO dissociation (eq 14) or CO catalysis (eq 15) and to add evidence against $Cr(CO)_3$ dissociation.

$$ (14) $$

$$ (15) $$
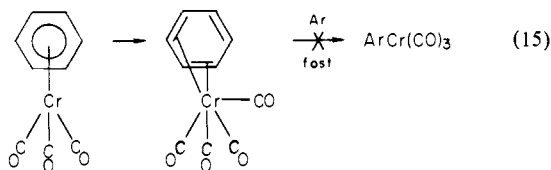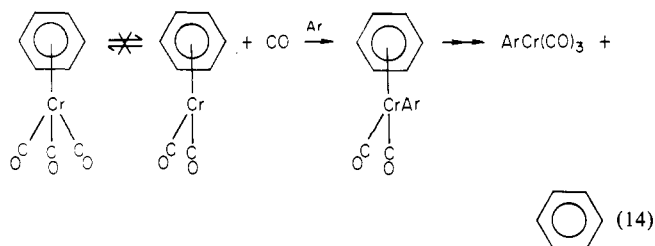
However, both the disappearance of ^{13}CO from the complexes at long reaction time and the production of $Cr(CO)_6$ show that

the complex reacts with CO at a rate which is comparable to the rate of arene exchange. Current, and somewhat inconclusive, evidence suggests that there are independent pathways.

$$ (16) $$

$$ (17) $$
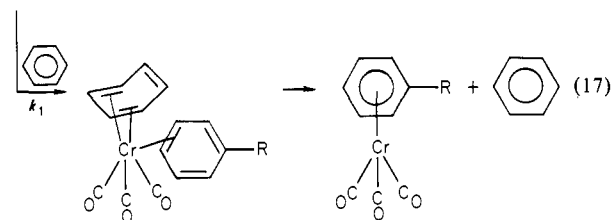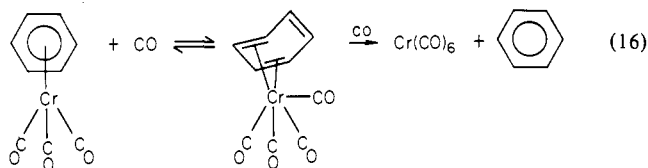
The first step of reaction 16 or 17 could involve either an $\eta^6 \rightleftharpoons \eta^4$ equilibrium (reaction 18) or a direct displacement (k_1 or k_2).

$$ (18) $$
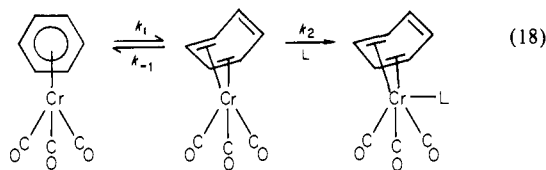
Although we have no evidence that requires eq 18, it provides a convenient rationale for reactions of the very reactive complexes in a process that is independent of arene concentration. If $k_{-1} \gg k_2$ then the reaction depends upon arene. Consider the compounds that undergo rapid exchange, naphthalene[7c] and benzyl cations.[24] In both cases illustrated the η^4 complex would be

$$ (19) $$

$$ (20) $$
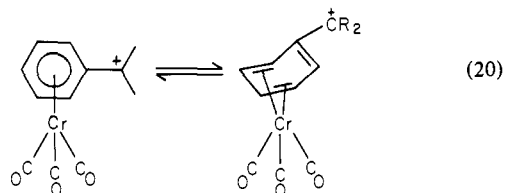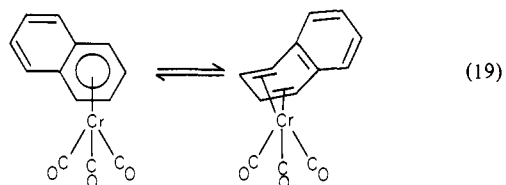
expected to be much more stable relative to the η^6 complex than in the case of the benzene complex η^6 to η^4 conversion. Therefore, these compounds might have a relatively low value of k_{-1} and react in a first-order fashion. (Benzene)tricarbonylchromium, on the other hand, would tend to collapse very rapidly to the η^6 complex, thus having $k_{-1} \gg k_2$ and reacting in a second-order fashion.

We have recently observed accelerated displacement of styrene from its tricarbonylchromium complex, which agrees with this postulate and with recent calculations of Albright et al.[25] The trapping of a η^4-naphthalene-THF complex at low temperature, reported by Cais,[26] would also fit in with this postulate.

We will discuss our results in terms of the fluxional process of eq 18 although they are also accommodated by mechanisms which omit this step.

(21) Brown, D. A.; Gogan, N. J.; Sloan, H. *J. Chem. Soc.* **1965**, 6873–6875.

(22) Gracey, D. E. F.; Jackson, W. R.; McMullen, C. H.; Thompson, N. *J. Chem. Soc. B* **1969**, 1197–1203.

(23) (a) Boneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220–1221. (b) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schultefrohlinde, D.; Koener on Gustorf. E. *J. Organomet. Chem.* **1974**, *69*, 259–269.

(24) (a) Trahanovsky, W. S.; Wells, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 5870–5871. (b) Meyer, A.; Jaouen, G. *J. Organomet. Chem.* **1975**, *97*, C21–C23.

(25) Albright, T. A.; Hoffman, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396–3411.

(26) Cais, M.; Kohn, D. H.; Lapid, A.; Tatarsky, D.; Dabard, R.; Jaouen, G.; Simmoneaux, G. *J. Organomet. Chem.* **1980**, *184*, 91–101.

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Catalyzed Arene Exchange. Willeford's results[10] and the present study show that cyclohexanone acceleration is first order in cyclohexanone and independent of arene concentration even at 0.2 M cyclohexanone concentration. This is a simple nucleophilic catalysis[27] in which a lone pair nucleophile reacts with the (arene)tricarbonylchromium complex to form a reactive species, as suggested by Mahaffy and Pauson. We can interpret this result in terms of the scheme given above. In this case the catalyst L reacts more rapidly than arene but still has a rate below that of k_{-1} thus showing concentration dependence.


(21–24)
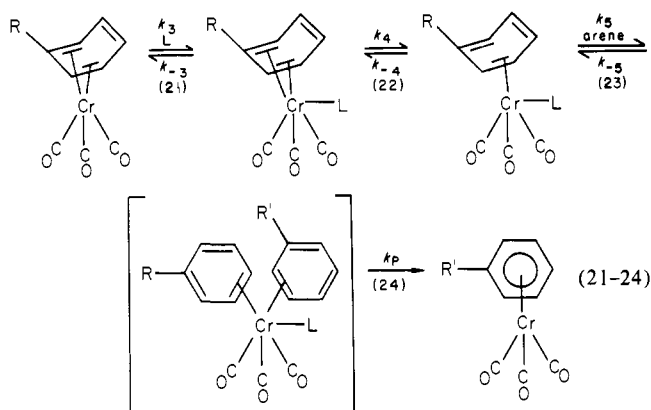
Our results would be consistent with replacement of the arene to give $L_3Cr(CO)_3$ such as observed with the three-phase test. This must be the pathway for that exchange. But the simple theory does not explain the tetrahydrofuran results of Strohmeier.[7b] Although greatly accelerated, the rate in tetrahydrofuran is still proportional to arene concentration. This suggests that even k_3/k_{-3} is rapidly reversible for tetrahydrofuran. Alternatively, eq 23 may be written as a displacement of L by incoming arene.

We also have some evidence for catalyzed neighboring group arene participation which is in accord with this mechanism.[28] Other aspects of this more complex scheme are discussed below.

The catalytic constants for the various catalysts studied so far are not known accurately. We have assembled approximate values in Table V from stated half-lives of the reactions at 170 °C by dividing by catalyst concentration and dividing this second-order rate constant by the first-order rate constant under the same conditions without catalyst. Since the data are for different reactions, they can only give an approximate idea of catalyst efficiency.

It can be seen that the relative effectiveness of catalysts is ketones $\sim$ nitriles > ethers, a series which follows their nucleophilicities. The low efficiency of THF also explains its reversible addition resulting in simultaneous THF and arene dependence. Possible methods of trapping L_1 and L_2 intermediates are under investigation.
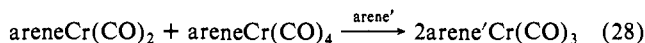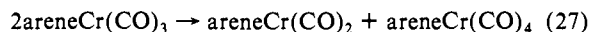

(25)

(26)
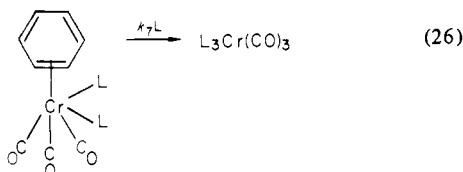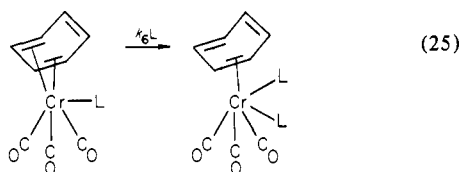
(Arene)carbonylchromium-Catalyzed Exchange. Based upon his conclusion that there was a term in the rate law for (arene)tricarbonylchromium self-exchange with ^{14}C arene which is

(27) Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969.

(28) Traylor, T. G.; Goldberg, M. J., submitted for publication.

Table V. Acceleration of Arene Exchange Reactions by Catalysts

catalyst	$k_{cat}/k_{uncat}{}^a$	catalyst	$k_{cat}/k_{uncat}{}^a$
PhCN	600	THF	30
cyclooctadiene	200	cyclohexanone	1300
diglyme	200	HMB complex[b]	30

[a] The observed rate was divided by catalyst concentration and by the uncatalyzed rate under otherwise identical conditions. Units are M^{-1}. *[b]* (Hexamethylbenzene)tricarbonylchromium.

second order in the complex (eq 5), Strohmeier suggested the bimolecular mechanism shown in eq 7.[7a] This postulate has received some criticism[8] and has been suggested to be excluded by the work of Jackson[23] and Mahaffy and Pauson,[8] as previously discussed. Mahaffy and Pauson suggested a bimolecular CO transfer leading to two species, either of which might undergo rapid exchange.

$$2areneCr(CO)_3 \rightarrow areneCr(CO)_2 + areneCr(CO)_4 \quad (27)$$

$$areneCr(CO)_2 + areneCr(CO)_4 \xrightarrow{arene'} 2arene'Cr(CO)_3 \quad (28)$$

Actually, the first difficulty is with Strohmeier's kinetic order. His kinetic expression implies a term which is second order in reactant (see eq 5). However, he plots log $(d[X]/dt)_0$ against $[X_0]$ where [X] is his (arene)carbonylchromium reactant.[7] Such initial rate measurements cannot distinguish the two reaction orders shown below where Y = product (arene)tricarbonylchromium because at zero time, $Y = 0$ and the two equations are identical.

$$(d[X]/dt)_0 = k_{II}[X]^2 \quad (29)$$

$$(d[X]/dt)_0 = k_{II}[X]([X] + [Y]) \quad (30)$$

We actually measure the disappearance of X separately from the appearance of Y and therefore differentiate these two expressions of the kinetic order. The reaction is *not* second order in reactant as implied. First, we find the reaction of mesitylene with (benzene)tricarbonylchromium to be cleanly first order in the complex (i.e., ln (complex) = $kt + c$) even at low mesitylene concentration where the "second-order" term (k_{II}) dominates. Second, the exchange of (p-xylene)tricarbonylchromium with benzene is first order in p-xylene complex (ln (p-xylene complex) vs. *t*) and directly proportional to the concentration of added (hexamethylbenzene)tricarbonylchromium.[20] It is noteworthy that at 0.1 M of the latter complex, although it does not exchange, almost all of the reaction is carried by its catalysis. Therefore, we can write the $k_{II}[X]^2$ term of Strohmeier with confidence as

$$d[X]/dt = k_{II}[X][total \ areneCr(CO)_3] \quad (31)$$

This finding eliminates the bimolecular mechanism proposed by Strohmeier.[7a] Thus the so-called bimolecular (arene)tricarbonylchromium reaction is simply another case of nucleophilic catalysis of arene exchange[8] for which we propose the mechanisms in eq 32 and 33.
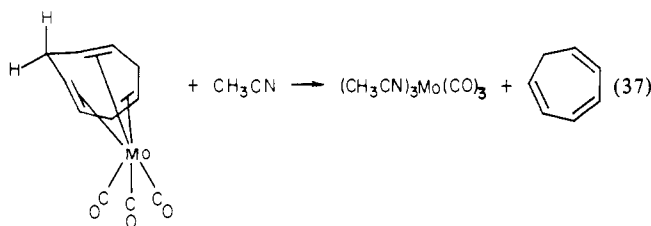

arene(CO)$_3$ (32, 33)
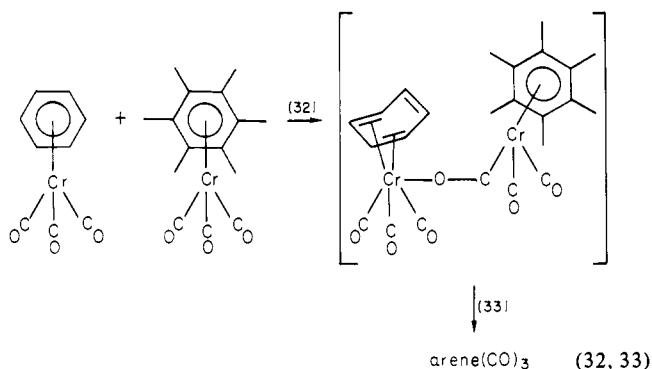
The possible formation of μ-carbonyl-bridged species is under investigation. As catalysts, these complexes are roughly equivalent to tetrahydrofuran.

There exists the possibility that we have oversimplified this process. Strohmeier[7b] observed that tetrahydrofuran greatly increased the rate, but the second-order term remains. This means

that these two catalysts are not competitive but somehow both participate at once. We tentatively suggest, in keeping with the discussion of the THF results above, that the (arene)carbonylchromium catalysts trap the reversibly formed THF adduct more efficiently than does arene itself.
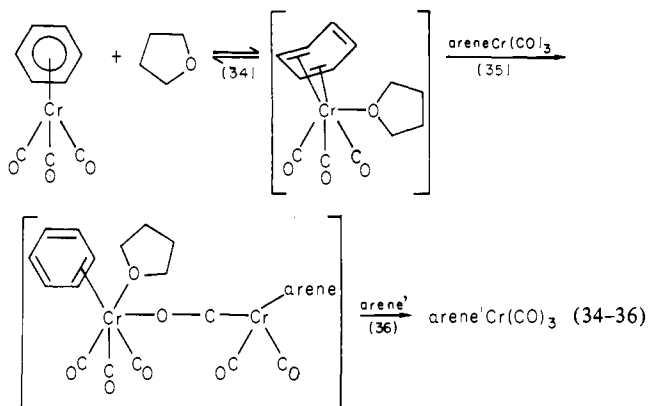
The intermediate species could also be $L_3Cr(CO)_3$ where the L's are both catalysts. This postulate implies a catalytic process which is second order in single catalysts, and such behavior has not yet been demonstrated in arene exchange. However, Al-Kathumi and Kane-Maguire[29] reported that a similar process (eq 37) is second order in acetonitrile.

Conclusions

Our results are consistent with a simple stepwise displacement of arenes in which there is essentially one mechanism involving a fluxional starting complex. The ligand L can be an arene, CO, or any of the catalysts mentioned above including the carbonyl of another (arene)tricarbonylchromium complex. This mechanism

(16, 21, 38)
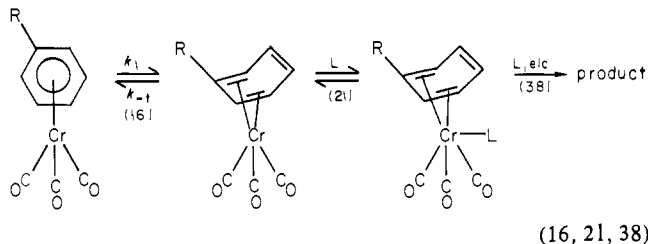
can include the further reaction with L to give $L_2areneCr(CO)_3$ and finally $L_3Cr(CO)_3$. Any of these intermediates could react with another arene, making details of this mechanism look complicated. We suggest that all of the reactions studied could be represented by the stepwise, reversible reaction of an arene L leading to $L_3Cr(CO)_3$, where each intermediate can react with other electron pair donors.

This mechanism implies new processes such as neighboring group participation by an arene or other nucleophiles in arene exchange.[28] These processes and other catalytic reactions are under study.

(29) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1974**, 428.

Organolanthanide and Organoyttrium Hydride Chemistry. 6. Direct Synthesis and ^1H NMR Spectral Analysis of the Trimetallic Yttrium and Yttrium–Zirconium Tetrahydride Complexes, {[(C5H5)2YH]3H}{Li(THF)4} and {[(CH3C5H4)2YH]2[(CH3C5H4)2ZrH]H}[1]

William J. Evans,*[2] James H. Meadows, and Timothy P. Hanusa

Contribution from the University of California, Irvine, Irvine, California 92717, and the University of Chicago, Chicago, Illinois 60637. Received September 19, 1983

Abstract: Improved syntheses for the trimetallic tetrahydride complexes {[(C5H5)2LnH]3H}{Li(THF)4} were investigated by studying the reactions of [(C5H5)2YH(THF)]2 with LiH, CH3Li, and t-C4H9Li. The t-C4H9Li reaction generates the trimer, {[(C5H5)2YH]3H}{Li(THF)4}, in 75% yield with (C5H5)2Y(t-C4H9)(THF) and (C5H5)3Y(THF) as byproducts. The reaction of [(C5H5)2YD(THF)]2 with t-C4H9Li forms the perdeuterio trimer, {[(C5H5)2YD]3D}{Li(THF)4}. The latter synthesis indicates that the *tert*-butyl group does not provide an H⁻ ion for the trimer. A mechanism for formation of the trimer by in situ generation of a (C5H5)2YH2⁻ intermediate which reacts with the dimeric hydride starting material to give the trimer is described. This mechanism was tested by reacting [(CH3C5H4)2ZrH2]2 with [(CH3C5H4)2YH(THF)]2 to form the heterometallic tetrahydride {[(CH3C5H4)2YH]2[(CH3C5H4)2ZrH]H}. The ^1H NMR spectra of {[(C5H5)2YH]3H}{Li(THF)4} and {[(CH3C5H4)2YH]2-[(CH3C5H4)2ZrH]H} are presented and the HH, YH, and YY coupling constants are discussed on the basis of computer simulation of the spectra.

As part of our general investigation of the chemistry of complexes containing lanthanide–hydrogen and yttrium–hydrogen

bonds,[3–7] we recently reported the synthesis of the novel trimetallic polyhydrides {[(C5H5)2ErH]3Cl}{Li(THF)4} (**1**) and {[(C5H5)2-